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(54) PROCESS FOR THE PREPARATION OF 2,6 DIALKYL PHENOLS

(71) We, JAPAN GAS CHEMICAL COMPANY INC., a Japanese Company, of No. 1—1, 2-chome, Uchisaiwai-cho, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of 2,6-dialkyl phenol. More particularly, the invention relates to a process for the production of a 2,6-dialkyl phenol comprising reacting a 2,6-dialkyl-4-t-alkyl phenol with a t-alkyl group acceptor in the presence of a Friedel-Crafts catalyst. In addition the invention concerns a process whereby a 2,6-dialkyl phenol is produced from a 1,3-dialkyl-5-t-alkyl benzene.

It is known that 2,6-dialkyl phenols are used as starting materials for the synthesis of polyphenylene oxide which is a thermoplastic synthetic resin having excellent mechanical, electrical, and heat resisting properties. Of these, 2,6-dimethyl phenol is the most desirable starting material and certain processes have been proposed for its production. The prior processes for the production of 2,6-dialkyl phenols will be considered in connection with 2,6-dimethyl phenol as an example, since it has been most frequently investigated.

According to a process using cyclohexanone as the starting material (French Patent No. 1,377,943), cyclohexanone and formaldehyde are reacted at 350°C. over a calcium phosphate catalyst carried on animal charcoal, and the resultant product is subjected to steam distillation to obtain 2,6-dimethyl phenol. However, this process gives a poor yield and the content of 2,6-dimethyl phenol in the distillate is as small as 64.5% entailing more than 30% of by-products (2,4,6-trimethyl phenol, o-cresol), so that it is not efficient as an industrial process.

According to a patent dealing with the alkylation of phenol (Belgian Patent No. 673,773), phenol is reacted with methanol or dimethyl ether at an elevated temperature in the presence of a catalyst comprising an oxide of an amphoteric metal such as aluminium to form 2,6-dimethyl phenol. In this process, however, the product after the removal of unreacted phenol by distillation contains a significant amount of o-cresol which can be as high as 61%, and the 2,6-dimethyl phenol is formed more as a by-product in an amount of only 30% together with unavoidable byproducts having methyl radicals at other than the 2,6-positions. Thus, this process is also impractical from the industrial viewpoint since it requires a complicated purification system in order to obtain highly pure 2,6-dimethyl phenol and the yield is too poor to be economical.

In a process described in Dutch Patent No. 6,506,830, (Chemical Abstracts 65 2173c) the alkylation of phenol is performed by a method whereby the yield of 2,6-dimethyl phenol is somewhat improved, but this process also suffers from the formation of byproducts similar to those in the above-mentioned Belgian Patent No. 673,773. There are also certain patents (Dutch Patent No. 285,017 (Chemical Abstracts 61 16017d), French Patent No. 1,396,197, and a French Patent No. 1,420,183) concerning the separation of byproducts in order to obtain 2,6-dimethyl phenol of high purity. However, these patents state in the specifications that 2,6-dimethyl phenol must be separated from cresol isomers, using complicated procedures.

Methylation of phenol is one of the known processes for producing 2,6-dimethyl phenol, but phenol exhibits an orientation effect in its substitution reaction with a cationic type reagent towards the ortho- and para-positions to the oxygen-bearing position. Accordingly, it is difficult to selectively methylate at the 2,6-positions alone in the methylation of phenol, and it is therefore impossible to avoid the formation of o-cresol, 2,4-dimethyl phenol and similar byproducts besides the desired 2,6-dimethyl phenol. Further methylation of o-cresol formed as a byproduct, to obtain additional 2,6-dimethyl phenol, may be possible, but the formation of byproducts having methyl radicals other than 2,6-positions is unavoidable in this case too.

Thus, conventional processes involving nuclear alkylation of phenol or a compound capable of being converted into phenol are not desirable for the industrial production of 2,6-dialkyl phenols.

Other possible synthetic methods to be employed for the production of 2,6-dialkyl phenols may involve the use of m-xylene, taking 2,6-dimethyl phenol as an example, as the starting material. This method may comprise sulphonating m-xylene in a conventional manner followed by alkali fusion to lead to the formation of 2,6-dimethyl phenol, in a manner similar to the synthesis of phenol from benzene. In this case, however, the formation of 2,4-dimethyl benzene sulphonic acid predominates as the sulphonation product and the formation of the desired 2,6-dimethyl benzene sulphonic acid is almost nil due to steric hindrance effects.

In order to obviate such difficulties in the formation of undesirable position isomers, the introduction of suitable bulky protective groups, before the reaction, to appropriate positions for the desired reaction, is generally effective.

One possible method for the production of 2,6-dialkyl phenol of high purity by the use of suitable bulky protective groups while avoiding the formation of troublesome byproducts, comprises the use of 2,6-dialkyl-4-t-alkyl phenols as the starting material and successive elimination of t-alkyl groups therefrom.

This process is disclosed in Dutch Patent No. 290,847 (Chemical Abstracts 62 2738f) concerning the synthesis of 2,6-dimethyl phenol in which 2,6-dimethyl-4-t-butyl phenol is freed from the t-butyl group to form 2,6-dimethyl phenol. The process disclosed in this patent comprises contacting a mixture of 2,6-dimethyl-4-butyl phenol and benzene with a catalyst at 400°C. in a nitrogen stream to effect the removal of the t-butyl group, thus producing 2,6-dimethyl phenol from 2,6-dimethyl-4-t-butyl phenol. This process, however, forms such byproducts as cresol and position isomers of 2,6-dimethyl phenol, though in a small proportion, owing to high temperature gaseous reaction, and therefore is disadvantageous when taking into consideration the uneconomically high reaction temperature. This process cannot be said to be industrially advantageous because the protective group introduced so as to avoid the production of undesirable position isomers is eliminated, in the final step, only in the form of an olefin. For instance, when a t-butyl group is used as the protective group and it is thereafter eliminated in the form of isobutylene, the t-butylation of the material m-xylene must be conducted by the use of free isobutylene itself or after converting iso-butylene into t-butylating agents such as t-butyl chloride.

Hence it will be appreciated that these conventional processes used for the production of 2,6-dialkyl phenol have various drawbacks, though each has its own advantageous features, but they do not provide a highly efficient process for the industrial production of 2,6-dialkyl phenol.

The present invention provides an improved process for the production of highly pure 2,6-dialkyl phenol in high yields from 2,6-dialkyl-4-t-alkyl phenol. It also provides a process for the production of highly pure 2,6-dialkyl phenol in high yields from 2,6-dialkyl-4-t-alkyl phenol wherein the process for the production of 2,6-dialkyl-4-t-alkyl phenol and the use of 1,3-dialkyl benzenes as the acceptor for the t-alkyl groups of the 2,6-dialkyl-4-t-alkyl phenol are combined.

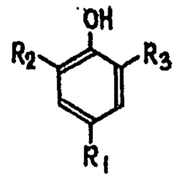
An object of this invention is to provide a process for the production of 2,6-dialkyl phenol of high purity and in an excellent yield.

It has now been found that 2,6-dialkyl phenols of high purity can be produced being substantially free from undesirable isomers, without requiring complicated purification steps, by the reaction of 2,6-dialkyl-4-t-alkyl phenol with t-alkyl group acceptors in the presence of a Friedel-Crafts catalyst at a relatively low temperature.

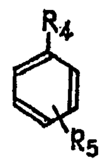
In the process of this invention, the elimination of the t-alkyl group from the 2,6-dialkyl-4-t-alkyl phenol to form the 2,6-dialkyl phenol can be carried out at a low temperature in the presence of a Friedel-Crafts catalyst due to the presence of a t-alkyl group acceptor which transfers the t-alkyl group alone preferentially and selectively to itself. Since the formation of byproducts such as position isomers of 2,6-dimethyl phenol due to the rearrangement of such primary alkyl groups as the methyl group can thus

be avoided, efficient production of 2,6-dialkyl phenol having high purity can be attained.

Accordingly the present invention provides a process for the production of a 2,6-dialkyl phenol which comprises reacting a 2,6-dialkyl-4-t-alkyl phenol having the formula

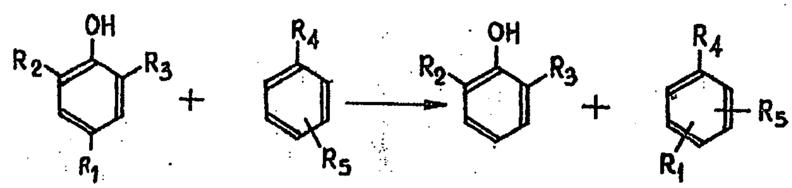


with an aromatic hydrocarbon having the formula



in the presence of a Friedel-Crafts catalyst at a temperature from −20 to 100°C to transfer the t-alkyl group to said aromatic hydrocarbon, wherein R_1 denotes a C_{1-7} t-alkyl group, R_2 and R_3 each denotes C_{1-4} normal alkyl groups, and R_4 and R_5 each denotes either hydrogen or a C_{1-4} normal alkyl group located mutually in o- or m-position when neither R_4 nor R_6 is hydrogen.

The reaction of the process of the invention is illustrated in the following equation:



The t-alkyl group, i.e. R_1, in the 2,6-dialkyl-4-t-alkyl phenol to be used as the material for the production of 2,6-dialkyl phenol is a group having a tertiary carbon atom such as t-butyl, t-amyl, t-hexyl, or t-heptyl, and is preferably a t-butyl group for economic reasons.

The t-alkyl-group acceptors suitable comprise aromatic hydrocarbons such as benzene, toluene, ethyl benzene, o-xylene and m-xylene. Those having a high electron density on the aromatic ring, i.e., those having more than one alkyl substituent, are advantageous owing to their high reactivity, and the use of m-xylene is preferable in practice.

The catalyst to be used in the process of this invention for the t-alkyl group transfer reaction can include such Friedel-Crafts catalysts as boron trifluoride, anhydrous aluminium chloride, anhydrous aluminium bromide and hydrogen fluoride. A mixture of these compounds may be used too. From the practical viewpoint, anhydrous aluminium chloride is preferred.

The process of this invention may be carried out in the presence of a solvent, particularly substances which do not react with the compounds present in the reaction system of this invention, such as saturated hydrocarbons. However, the use of such solvents is generally unnecessary since the t-alkyl group acceptor to be used in the process of this invention may itself serve as the solvent.

The process of this invention may be carried out as follows. The requisite amount of the 2,6-dialkyl-4-t-alkyl phenol (e.g., 2,6-dimethyl-4-t-alkyl phenol) is added, with stirring, to the above-mentioned t-alkyl group acceptor (e.g. m-xylene) kept at a temperature of from −20°C. to 100°C. and reacted in the presence of a Friedel-Crafts catalyst for the period of from 30 minutes to 6 hours.

One of the most characteristic features of the process of this invention lies in the production of 2,6-dialkyl phenol of high purity by the use of the t-alkyl group acceptor so as to permit the reaction at lower temperature and thereby inhibit the formation of byproducts due to rearrangement of the alkyl groups such as the methyl group. Accordingly, the reaction is preferably conducted at a temperature in the range of from −20 to +30°C., and preferably between −5°C. and 15°C.

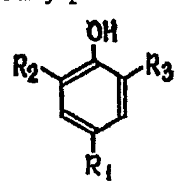
In order to separate the catalyst from the reaction mixture after the completion of the t-alkyl group transfer reaction, various methods may be employed depending upon the catalyst used, including the decomposition of the catalyst by the addition of water, distillation to remove the catalyst, separation and extraction of the catalyst in the case of phase separation, and the decomposition of the complex when a complex is formed.

The treatment of the reaction mixture after the separation of the catalyst varies depending upon the t-alkyl acceptor used in the reaction and the number of carbon atoms in the alkyl groups in the 2,6-dialkyl-4-t-butyl phenols employed. When m-xylene is reacted with 2,6-dimethyl-4-t-alkyl phenol, for example, first the m-xylene is distilled out from the catalyst-free reaction mixture followed by the separation of 2,6-dimethyl phenol from 5-t-alkyl-m-xylene. In this case, the separation of 2,6-dimethyl phenol from 5-t-alkyl-m-xylene is conducted by distillation, or a combination of steps involving first extracting the 2,6-dimethyl phenol from a fraction of the mixture of 2,6-dimethyl phenol and 5-t-alkyl-m-xylene obtained after simple distillation, with aqueous alkali solution to form its alkali salt, then acidifying the alkaline aqueous phase and thereby separating out the 2,6-dimethyl phenol which is thereafter collected by filtration. By treatment in this manner, i.e., when the separation of 2,6-dimethyl phenol from 5-t-alkyl-m-xylene is difficult using simple distillation only, depending upon the kind of the t-alkyl group in the 2,6-dimethyl-4-t-alkyl phenol used as the material, the separation of both is easily effected by extracting 2,6-dimethyl phenol from a fraction of the mixture of 2,6-dimethyl phenol and 5-t-alkyl-m-xylene obtained after simple distillation with alkali solution in the form of its alkali salt, and by crystallising out 2,6-dimethyl phenol from its acidic solution to give pure 2,6-dimethyl phenol after filtration. In addition, the separation of 2,6-dimethyl phenol from the reaction mixture after t-alkyl transfer reaction may be effected by first adding alkali to the reaction mixture from which the catalyst has been or has not been removed, to convert the 2,6-dimethyl phenol into its alkali salt, then removing m-xylene and 5-t-alkyl-m-xylene by steam distillation, acidifying the remaining aqueous solution, and finally collecting the 2,6-dimethyl phenol by filtration as it crystallises out.

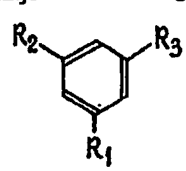
The 2,6-dialkyl phenols obtained in accordance with the process of this invention are of such excellent high purity that almost no impurities can be detected by gas chromatographic analysis, nor can any position isomers, (for example, 2,4-dialkyl phenols), be observed.

In this way, the process of this invention has advantages in that high purity 2,6-dialkyl phenols are obtained in good yield at a lower reaction temperature without requiring troublesome purification step procedures, by simply reacting 2,6-dialkyl-4-t-alkyl phenol with the t-alkyl group acceptor in the presence of a Friedel-Crafts catalyst.

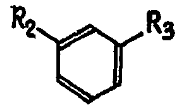
2,6-dialkyl-4-t-alkyl phenols can be obtained by many conventional methods, but they are most advantageously obtained from 1,3-dialkyl-5-t-benzenes. In this case, the invention provides a process for the production of a 2,6-dialkyl phenol which comprises a first step in which a 2,6-dialkyl-4-t-alkyl phenol having the formula



is prepared from a 1,3-dialkyl-5-t-alkyl benzene having the formula

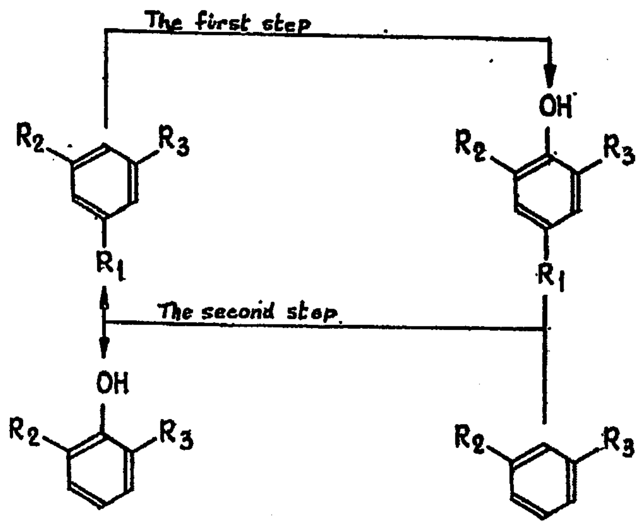


a second step in which the 2,6-dialkyl-4-t-alkyl phenol is reacted with a 1,3-dialkyl benzene having the formula



in the presence of a Friedel-Crafts catalyst at a temperature of −20 to 100°C to form the 2,6-dialkyl phenol and the 1,3-dialkyl-5-t-alkyl benzene, and circulating the 1,3-dialkyl-5-t-alkyl benzene obtained in the second step to the first step for reuse, wherein R_1 denotes a C_{4-7} t-alkyl group, and R_2 and R_3 each denotes a C_{1-4} normal alkyl group.

This reaction is illustrated as follows:



In the first step, the 1,3-dialkyl-5-t-alkyl benzene is converted into a 2,6-dialkyl-4-t-alkyl phenol. Then, in the second step, the 2,6-dialkyl-4-t-alkyl phenol thus obtained is reacted in the presence of a Friedel-Crafts catalyst with a 1,3-dialkyl benzene to transfer the t-alkyl group to the 1,3-dialkyl benzene to give the 2,6-dialkyl phenol (the desired product) together with the 1,3-dialkyl-5-t-alkyl benzene which is circulated to the first step.

In preparing the 1,3-dialkyl-5-t-alkyl benzene to be used in the first step, the t-alkyl group can be introduced into the 1,3-dialkyl benzene in the following manner, taking 5-t-alkyl-m-xylene as an example. The t-alkyl group is always introduced in a position not adjacent to the methyl groups of m-xylene owing to the steric effects between the methyl groups of m-xylene and the t-alkyl group to be introduced, and hence preferential formation of 5-t-alkyl-m-xylene is attained. The step of obtaining 2,6-dialkyl-4-t-alkyl phenol from the 1,3-dialkyl-5-t-alkyl benzene (the first step) can be carried out by the combination of steps comprising first sulphonating the 1,3-dialkyl-5-t-alkyl benzene to form selectively 2,6-dialkyl-4-t-alkyl benzene sulphonic acid, then converting this into 2,6-dialkyl-4-t-alkyl phenol by alkali fusion or by chlorinating the 1,3-dialkyl-5-t-alkyl benzene to form selectively 2,6-dialkyl-4-t-alkyl chlorobenzene which is thereafter hydrolysed to 2,6-dialkyl-4-t-alkyl phenol. In addition, 1,3-dialkyl-5-t-alkyl benzene may be directly oxidised to 2,6-dialkyl-4-t-alkyl phenol. Thus, the phenolation at the position between the two alkyl groups may be performed by any suitable method.

The first step will now be explained in more detail taking the sulphonation of 5-t-alkyl-m-xylene followed by its alkali fusion as an example.

In the sulphonation of 5-t-alkyl-m-xylene, it is possible to introduce the sulphonic

acid group on to the position between the two methyl groups, to which it is usually impossible to introduce such a sulphonic acid group, owing to the steric effect of the bulky t-alkyl group. Moreover, the t-alkyl group in this case serves not only to act as a simple protective group but also to enhance the electron density and also to facilitate the sulphonation reaction. The later alkali fusion is carried out in a conventional manner, and the use of potassium hydroxide or a mixture of potassium hydroxide and sodium hydroxide is preferred.

The second step, where the 2,6-dialkyl phenol and 1,3-dialkyl-5-t-alkyl benzene are obtained from the 2,6-dialkyl-4-t-alkyl phenol and 1,3-dialkyl benzene, is explained in more detail taking 2,6-dimethyl-4-t-alkyl phenol as an example.

Instead of eliminating the t-alkyl group simply as the corresponding olefin (for instance as isobutylene from t-butyl group) from the 2,6-dimethyl-4-t-alkyl phenol, it is now possible to obtain 2,6-dimethyl phenol together with the 5-t-alkyl-m-xylene to be used as an intermediate material by reacting m-xylene as the t-alkyl group acceptor in the presence of a Friedel-Crafts catalyst to effect the transfer of the t-alkyl group to the m-xylene.

The 5-t-alkyl-m-xylene thus regenerated can be circulated and reused as the material for the first reaction step, so that the 1,3-dialkyl-5-t-alkyl benzene itself (in this example, 5-t-alkyl-m-xylene) is only required at the start of the reaction, and further additions are substantially unnecessary thereafter owing to the regeneration of the said compound.

By the above-mentioned combination of these steps, the production of 2,6-dialkyl phenol is now possible by using a 1,3-dialkyl-5-t-alkyl benzene as the starting material for obtaining the 2,6-dialkyl-5-t-benzene and by using a 1,3-dialkyl benzene as the acceptor for the t-alkyl group thus involving the introduction of a suitable protective group to prevent the formation of position isomers and also enhancing the yield of the desired compound, and also involving the simultaneous introduction and elimination of the protective group as well as the re-use of the protective t-alkyl group by circulation to the first stage of the reaction.

This combination of steps provides a most desirable process for the production of high purity 2,6-dialkyl phenol from a 1,3-dialkyl-5-t-alkyl benzene by the combination of highly efficient transfer reactions.

The advantages of the above-described process may be further enumerated as follows:

(1) The yield of intermediate and final products are selectively enhanced by the prevention of the formation of undesirable position isomers by the introduction of a suitable protective group.

(2) Separation and purification of the intermediate and final products are very simple and easy.

(3) The protective group introduced can be re-used by circulation to the next cycle, owing to the one step reaction involving the elimination of the protective group introduced and the introduction thereof in the next cycle.

(4) The raw materials are available inexpensively and in high purity, such as m-xylene when producing 2,6-dimethyl phenol.

The process of this invention will be more fully described in the following illustrative explanation.

The 1,3-dialkyl-5-t-alkyl benzene to be used as the starting material for obtaining the 2,6-dialkyl-4-t-alkyl phenol can be obtained, taking 5-t-alkyl-m-xylene as an example, as follows. When using the t-butyl group as a protective group, which is the most useful of the t-alkyl groups containing 4—7 carbons, isobutylene may be used as a t-butylating agent. In this case, any conventional methods for introducing the t-butyl group may be employed, for instance, introduction of isobutylene into a mixture of m-xylene and sulphuric acid, passing isobutylene together with m-xylene over a solid phosphoric acid catalyst, condensation of isobutylene with m-xylene by using such catalysts as hydrogen fluoride, aluminium chloride and ferric chloride, or reaction of isobutylene with m-xylene using boron fluoride as a condensing agent. The t-butylation may be also carried out by using a t-butyl halide, e.g. t-butyl chloride. In this case, the use of aluminium chloride or ferric chloride is preferred as a condensing agent. The t-butylation may be effected also by the use of t-butanol using aluminium chloride, hydrogen fluoride, or sulphuric acid. Since the 1,3-dialkyl-5-t-alkyl benzene (in this example, 5-t-alkyl-m-xylene) so produced is regenerated in the second step and can be circulated for re-use, the t-butylation may be carried out only at the initial stage of the reaction.

The sulphonation and the following alkali fusion in the first step is carried out as follows, taking the production of 2,6-dimethyl-4-t-alkyl phenol from 5-t-alkyl-m-xylene

as an example. The sulphonation of 5-t-alkyl-m-xylene is conducted by using conventional sulphonating agents, such as concentrated sulphuric acid, 100% sulphuric acid, fuming sulphuric acid and sulphuric anhydride. Other sulphonating agents such as sulphamic acid and halosulphonic acids such as chlorosulphonic acid and fluorosulphonic acid, may be used as well, but the use of concentrated sulphuric acid or fuming sulphuric acid is the most desirable from the industrial viewpoint.

Since the 5-t-alkyl-m-xylene is very readily subjected to sulphonation, the sulphonation can be carried out at a temperature as low as 20—90°C. for a reaction period of 1—3 hours. The amount of such sulphonating agent to be used is usually 0.5—3 moles per mole of 5-t-alkyl-m-xylene. In order to separate excess sulphuric acid, when sulphuric acid is used as the sulphonating agent, it is possible to partially neutralise the sulphonated reaction mixture with sodium sulphite or sodium carbonate, then add calcium carbonate to neutralise excess acid and then fiter while hot the precipitate of calcium sulphate so formed.

However, it is preferred to use a procedure involving the steps of dissolving the sulphonated reaction mixture in water and adding thereto an excessive amount of sodium chloride, or adding the reaction mixture to a saturated sodium chloride aqueous solution to form sodium 2,6-dimethyl-4-t-alkyl benzene sulphonate which is thereafter recovered by filtration. In this case, it is also possible to salt out the sulphonated reaction mixture with sodium chloride after partially neutralising the reaction mixture with sodium sulphite or sodium carbonate.

The alkali fusion reaction of the resultant sodium 2,6-dimethyl-4-t-alkyl benzene sulphonate is carried out at a temperature of 310—400°C., preferably at 330—350°C., by using as the alkali potassium hydroxide, or a mixture of potassium hydroxide and sodium hydroxide. The amount of alkali to be used is preferably 5—25 moles per mole of sodium 2,6-dimethyl-4-t-alkyl benzene sulphonate. This alkali fusion is desirably conducted in an atmosphere of inert gas such as nitrogen because the formation of byproducts tends to become significant when the reaction is conducted in atmospheric air.

After the completion of this alkali fusion, the reaction mixture is dissolved in water and the resultant solution is neutralised with a mineral acid such as sulphuric acid or hydrochloric acid. It is also possible to effect the neutralisation by introducing carbon dioxide gas.

The neutralised reaction product forms a solid mass which is extracted with a water-immiscible solvent such as ether or benzene, and purified by distillation. Instead of extracting with an organic solvent, the crystals so formed may be recovered by filtration.

Where a 2,6-dialkyl phenol is produced by the chlorination of the aromatic nucleus followed by the hydrolysis to form phenol, the process will be explained in more detail on the basis of the use of m-xylene as the starting material. In this procedure, m-xylene is first converted, for example into 5-t-butyl-m-xylene, by a process as hereinbefore described. Then it is chlorinated with chlorine gas in the presence of a catalyst which is conventionally employed for the nuclear chlorination, for instance iodine, in an amount of from 0.01 to 1 mole per mole of 5-t-butyl-m-xylene, in a solvent such as carbon tetrachloride under cooling to form 2-chloro-5-t-butyl-m-xylene. After which said chlorobenzene derivative is hydrolysed at elevated temperature and pressure with a 10—15% aqueous solution of an alkali hydroxide, for instance at 320°C. under a nitrogen pressure of 300 atm. to give 2,6-dimethyl phenol, the desired product.

The second step comprises the reaction of 2,6-dialkyl-4-t-alkyl phenol with 1,3-dialkyl benzene. This reaction will now be illustrated, taking the reaction between 2,6-dimethyl-4-t-alkyl phenol and m-xylene as an example.

A mixture of 2,6-dimethyl-4-t-alkyl phenol, m-xylene, and the catalyst, is stirred at a temperature generally in the range of from −20°C. to +100°C., to effect the transfer reaction. The higher the reaction temperature, the less will be the yields of both 2,6-dimethyl phenol and 5-t-alkyl-m-xylene, due to the isomerisation reaction and other side reactions causing the formation of undesirable byproducts which tend to reduce the purity of the desired product to a considerable extent.

Hence, the reaction temperature is preferably selected within the range of −20°C. to +30°C., and more particularly in the range of −5°C to +15°C. This step may be carried out in the presence of a solvent which is not reactive with any one of the compounds to be used in the process of this invention, such as, for example, saturated aliphatic hydrocarbons.

However, the use of such a solvent is generally not necessary since the 1,3-dialkyl benzene, in this case m-xylene itself serves as a solvent.

Catalysts to be used for this reaction include a Friedel-Crafts catalyst such as anhydrous aluminium chloride, anhydrous aluminium bromide, boron trifluoride, or hydrogen fluoride. A mixture of these compounds may also be used as the catalyst. Practically, the use of hydrogen fluoride and aluminium chloride is the most preferable. The catalyst is added, in general, in the proportion of 0.2—6.0 moles per mole of the 2,6-dialkyl-4-t-alkyl phenol, in this case 2,6-dimethyl-4-t-alkyl phenol.

In order to separate the catalyst from the reaction mixture obtained after the t-alkyl group transfer reaction has taken place, any conventional procedure may be used involving the decomposition of the catalyst by the addition of water, distilling off the catalyst, separation of the catalyst when phase separation is applied, extraction of catalyst, decomposition of the complex when a complex is formed, and other appropriate methods for the catalyst used. For example, the separation of the catalyst by its decomposition with added water is conducted as follows.

The catalyst is decomposed by adding water, and then the water is separated out. After rinsing two or three times with water and then removing the water therefrom, the reaction mixture is distilled to remove m-xylene, then fractionated into 2,6-dimethyl phenol and 5-t-alkyl-m-xylene. The separation of 2,6-dimethyl phenol and 5-t-alkyl-m-xylene is carried out either by distillation, or by the extraction of a fraction comprising the mixture of 2,6-dimethyl phenol and 5-t-alkyl-m-xylene obtained after simple distillation, with the use of aqueous alkali solution to separate out 2,6-dimethyl phenol as its alkali salt, then acidifying the alkaline aqueous phase to crystallise out the 2,6-dimethyl phenol which is thereafter recovered by filtration. The separation of the 2,6-dimethyl phenol from the 5-t-alkyl-m-xylene is, in most cases, preferably carried out by fractional distillation, but sometimes, depending upon the size of the t-alkyl group contained in the 2,6-dimethyl-4-t-alkyl phenol used as the material of the transfer reaction, the complete separation becomes difficult by simple distillation alone. In such a case, it is possible readily to obtain the 2,6-dimethyl phenol and 5-t-alkyl-m-xylene in high purity according to a procedure involving simple distillation to form a fraction comprising a mixture of 2,6-dimethyl phenol and 5-t-alkyl-m-xylene, extracting 2,6-dimethyl phenol therefrom as its alkali salt, and acidifying the alkaline phase to separate out the 2,6-dimethyl phenol which is thereafter recovered by filtration. In addition, the separation of 2,6-dimethyl phenol from the transfer reaction product may be effected by first adding an alkali to the reaction product from which the catalyst has or has not already been removed, to convert the 2,6-dimethyl phenol into its alkali salt, then removing m-xylene and 5-t-alkyl-m-xylene by steam distillation, acidifying the remaining aqueous solution to separate out 2,6-dimethyl phenol in crystal form, and collecting the crystals by filtration.

The 2,6-dialkyl phenol thus obtained in accordance with the process of this invention has extremely high purity, and substantially no impurity is detectable by gas chromatographic analysis, the substantial absence of any position isomers of the 2,6-position (for example, 2,4-dialkyl phenols, etc.) having been observed.

Moreover, 1,3-dialkyl-5-t-alkyl benzene obtained in this way has also excellent purity and in which no impurity is detectable by gas chromatographic analysis. Hence, the 1,3-dialkyl-5-t-alkyl benzene can be directly circulated for re-use to the first step without any further purification.

As has already been mentioned, the process of this invention has excellent advantages in that the 2,6-dialkyl phenol is obtainable in high purity at a very good yield, using 1,3-dialkyl-5-t-alkyl benzene as the starting material, while avoiding the formation of undesirable position isomers and enhancing the yields of the intermediate and final products by the introduction of a protective group, and in the elimination of said protective group, simultaneously carrying out the elimination of the protective group together with the introduction of the protective group into the 1,3-dialkyl benzene by simply inserting a highly efficient t-alkyl group transfer step, and also re-using the t-alkyl group as the protective group, by circulation to the first step of the reaction, thus providing an integrated process which is suitable for the industrial production of 2,6-dialkyl phenol.

The process of this invention will be more fully described by reference to the following Examples in which the synthesis of 5-t-alkyl-m-xylene is shown as reference examples (preliminary step) and the production of 2,6-dialkyl phenol according to this invention is given in the Examples. The invention is not, of course, to be limited by these Examples.

Reference Example 1 (starting material)

Into a four-necked one litre flask made of copper and fitted with a stirrer, there was charged 317 g. (3.0 moles) of m-xylene, which had been analysed by a gas chroma-

tographic method to have a purity of at least 98%, and cooled to 0°C. by using an ice bath. Then 40 g. (2.0 moles) of liquid hydrogen fluoride were added as a catalyst, followed by mixing with agitation. To the resultant mixture was introduced 45 litres (N.T.P. 2.0 moles) of gaseous isobutylene with stirring for about three hours at such a feed rate that the temperature of the contents of the flask were kept within the range of 0—5°C.

After the introduction of gaseous isobutylene had been completed, the contents were further stirred and allowed to react for an additional four hours while keeping the temperature at 0—5°C.

After the completion of the reaction, the reaction mixture was poured on cracked ice, neutralised with an excess of potassium hydroxide, rinsed with water three times, and finally dried over calcium chloride.

The rinsed and dried reaction mixture was distilled to separate a fraction boiling at 136—141°C. (m-xylene) and a fraction boiling at 202—205°C. (5-t-butyl-m-xylene) to obtain 269 g. (1.67 moles) of 5-t-butyl-m-xylene.

This fraction boiling at 202—205°C. had a refractive index of $n_D^{20}=1.4961$ (literature B.P. 205°C./760 mm Hg, $n_D^{20}=1.4961$) and the infrared absorption spectrum also showed complete agreement with that of 5-t-butyl-m-xylene.

The yield of 5-t-butyl-m-xylene based on isobutylene was 85%.

Reference Example 2 (starting material)

Into a four-necked one litre flask fitted with a stirrer and dropping funnel, there was charged 510 g. (4.8 moles) of m-xylene having the same quality as used in the preceding Example, then 39 g. (0.24 mole) of anhydrous ferric chloride were added as the catalyst, and the whole was cooled to 0°C. 111 g. (1.2 moles) of t-butyl chloride were gradually dropped into the flask, while keeping the temperature at 0°C., at such a rate as not to cause any effective temperature rise in the contents of the flask. After the completion of this dropwise addition, the reaction product was combined with cooled water to decompose the catalyst. The contents were then placed in a separating funnel to separate water therefrom, and treated with a 5% aqueous alkali solution, rinsed with water three times, and then dried over calcium chloride. The rinsed and dried reaction mixture was distilled and fractionated in a manner similar to that employed in Reference Example 1 to give 158 g. (0.98 mole) of 5-t-butyl-m-xylene. $n_D^{20}=1.4961$. The yield of 5-t-butyl-m-xylene based on t-butyl chloride was 81%.

Reference Example 3 (starting material)

Into a four-necked one litre flask fitted with a stirrer and dropping funnel, 378 g. (3.56 moles) of m-xylene having the same quality as that used in Reference Example 1 were charged. Then 400 g. (3 moles) of anhydrous aluminium chloride were added and the mixture cooled to 0°C. Keeping the temperature of the contents at 0°C., a mixture of 111 g. (1.5 moles) of t-butanol and 100 g. (0.94 mole) of m-xylene was gradually dropped in at such a rate as not to cause any effective rise in temperature. After the addition was complete, stirring was continued for an additional three hours to complete the reaction while maintaining the temperature at 0—5°C.

After the completion of the reaction, the reaction mixture was treated in a manner similar to that employed in Reference Example 2 and distilled to give 229 g. (1.41 moles) of 5-t-butyl-m-xylene; $n_D^{20}=1.4961$. The yield of 5-t-butyl-m-xylene based on t-butanol was 94%.

Reference Example 4 (starting material)

A four-necked one litre flask fitted with a stirrer and dropping funnel was charged with 469 g. (3.5 moles) of m-diethyl benzene. 801 g. (3 moles) of anhydrous aluminium bromide were added as the catalyst and cooled to 0°C. While maintaining this temperature, a mixture of 132 g. (1.5 moles) of t-amyl alcohol and 134 g. (1.0 mole) of m-diethyl benzene was gradually added dropwise at such a rate as not to cause any effective rise in the temperature. After the dropwise addition had been completed, stirring was continued for an additional three hours while maintaining the temperature at 0—5°C. to complete the reaction. After the reaction had been completed, the reaction mixture was treated as in Reference Example 2 to give 266 g. (1.3 moles) of 5-t-amyl-m-diethyl benzene. The yield of 5-t-amyl-m-diethyl benzene based on t-amyl alcohol was 87%.

Example 1

A four-necked 200 cc flask fitted with a stirrer was charged with 81 g. (0.5 mole) of 5-t-butyl-m-xylene obtained according to the method of Reference Example 3, and

100 g. of 98% sulphuric acid were dropped into the flask with stirring. The temperature of the contents began to rise gradually soon after the addition of the sulphuric acid started. When the temperature of the contents reached 30°C., it was cooled with water and 98% sulphuric acid was continuously added while controlling the temperature at between 30 and 35°C. After the addition of the sulphuric acid had been completed, the reaction was continued for an additional hour while keeping the temperature of the flask contents at 30—35°C. until the reaction was completed.

The reaction mixture was then poured little by little into 450 cc.of water, with stirring, and dissolved therein. The resultant solution was stirred and 167 g. of salt (NaCl) were added thereto little by little to crystalise out while crystals from the solution. After allowing to stand for a while under cooling, the crystals so formed were suction- and compression-filtered, and rinsed twice with a small amount of saturated sodium chloride solution. The white solid mass so obtained was ground and dried at 110°C. to give 135 g. of white powder containing a small amount of sodium chloride. Recrystallisation of the powder from absolute alcohol followed by the removal of sodium chloride and drying gave 130 g. of white powder. The infrared absorption spectrum measured on these crystals confirmed that this was sodium 2,6-dimethyl-4-t-butyl benzene sulphonate and the yield of which based on 5-t-butyl-m-xylene was 98%.

Next, 281 g. (5 moles) of potassium hydroxide and 30 cc of water were put into a 400 cc nickel crucible and heated to an internal temperature of 300°C. Then 131 g. (0.5 mole) of the powder of the sodium 2,6-dimethyl-4-t-butyl benzene sulphonate were added little by little to the contents of the crucible while stirring with a copper rod. After all the powder had been added, stirring was further continued with additional heating. When the temperature reached 330°C., foaming took place with darkening of the melt and the mixture become fluid and apparently uniform. The mixture was further stirred for an additional ten minutes while maintaining the temperature at 330—350°C. to complete the reaction. Then the reaction mixture was cooled and added to 400 cc of water to dissolve therein. After the mixture had dissolved uniformly the solution was acidified with sulphuric acid, to crystallise out dark crystals which were then extracted with ether to separate the organic substances as an ether solution from the aqueous phase. The ether solution thus obtained was then freed from ether by distillation, and the residue was distilled under reduced pressure to give 74 g. of liquid boiling at 106—110°C. at 4 mmHg. The liquid readily crystallised into white crystals on standing. The crystal had a melting point of 79.5—80.5°C. and showed no depression of melting point when melted together with an authentic sample of 2,6-dimethyl-4-t-butyl phenol (m.p. 80—81°C.). The analysis by infrared absorption spectrum also identified the crystals as 2,6-dimethyl-4-t-butyl phenol. The yield based on sodium 2,6-dimethyl-4-t-butyl benzene sulphonate was 83%.

Next, a four-necked one litre copper flask fitted with a stirrer was charged with 382 g. (3.6 moles) of m-xylene and cooled to 0°C. by using an ice bath, then the flask was charged with 40 g. (2.0 moles) of liquid hydrogen fluoride as the catalyst and mixed by stirring. A solution of 214 g. (1.2 moles) of 2,6-dimethyl-4-t-butyl phenol obtained in the above procedure in admixture with 100 g. m-xylene was gradually added dropwise with stirring while keeping the temperature of the contents at 0—5°C. After the addition was complete, the stirring was continued for an additional 4 hours keeping the same temperature to complete the reaction. Then the contents were poured onto cracked ice, neutralised with sodium hydrogen carbonate, rinsed three times with water, and dried over anhydrous sodium sulphate. The resulting reaction mixture was distilled to remove a fraction boiling at 136—141°C. (m-xylene), and the remaining portion distilled under reduced pressure to obtain a fraction boiling at 78—85°C/6 mm Hg which was then transferred into a separating funnel and shaken with 600 cc of 10% aqueous sodium hydroxide solution followed by standing to separate into aqueous and organic phases. The organic phase thus obtained was washed with water, dried over calcium chloride, and analysed and found to have a refractive index of $n_D^{20}=$ 1.4961 which agreed with that of 5-t-butyl-m-xylene. The infrared absorption spectrum also agreed completely with that of 5-t-butyl-m-xylene. The yield of 5-t-butyl-m-xylene was 187 g. (1.15 moles), which corresponded to 96% based on 2,6-dimethyl-4-t-butyl phenol.

The aqueous phase treated with 10% aqueous sodium hydroxide was neutralised with sulphuric acid to separate out white crystals, which were filtered by suction, rinsed with a small amount of water, and vacuum dried, to give 139 g. of white crystals having a melting point of 47—49°C. (No depression of the melting point was observed when mixed with an authentic sample of m.p.=49°C.). The infrared absorption spectrum showed complete agreement with that of 2,6-dimethyl phenol. The yield of 2,6-dimethyl phenol based on 2,6-dimethyl-4-t-butyl phenol was 96%.

EXAMPLE 2

A four-necked 200 cc flask fitted with a stirrer was charged with 100 g. of 5% fuming sulphuric acid. 81 g. (0.5 mole) of 5-t-butyl-m-xylene obtained in the procedure of Example 1 (t-butyl group transfer reaction between 2,6-dimethyl-4-t-butyl phenol and m-xylene), were then gradually added dropwise with stirring. The temperature of the contents gradually rose during the addition of 5-t-butyl-m-xylene. After the temperature of the contents had reached 30°C., it was cooled with water and the dropwise addition of 5-t-butyl-m-xylene was continued while maintaining the temperature at 30—35°C. After the dropwise addition had been completed, the stirring was continued for a further hour, while maintaining the temperature of the contents at 30—35°C., to complete the reaction. The reaction mixture was then added little by little into 450 cc of saturated aqueous sodium chloride solution, with stirring, to form white crystals, which were then treated as in Example 1 to give 138 g. of a white powder containing a small amount of sodium chloride. This powder was recrystallised from absolute alcohol to free it from sodium chloride to give 130 g (0.492 mole) of white powder (sodium 2,6-dimethyl-4-t-butyl benzene sulphonate). The yield of sodium 2,6-dimethyl-4-t-butyl benzene sulphonate based on 5-t-butyl-m-xylene was 98%.

Next, a 400 cc nickel crucible was charged with 140 g. (2.5 moles) potassium hydroxide, 140 g. (3.5 moles) sodium hydroxide, and 350 cc of water, and heated. After the temperature of the contents reached 300°C., 131 g. (0.5 mole) of sodium 2,6-dimethyl-4-t-butyl benzene sulphonate obtained in the above procedure were added little by little while stirring the contents with a copper rod. After all the powder was added, it was heated more strongly with agitation. When the temperature of the contents reached 330°C, foaming took place with darkening of the contents which became fluid and uniform. After this the temperature of the contents was maintained at 330—350°C. for an additional 10 minutes to complete the reaction. The reaction mixture was then treated as in Example 1 to give 67 g. (0.376 mole) of 2,6-dimethyl-4-t-butyl phenol of m.p. of 77.5—80°C., which showed no melting point depression when compared with an authentic sample. The yield was 75%.

A four-necked one litre flask, fitted with a stirrer, was charged with 382 g. (3.6 moles) of m-xylene which had been analysed by gas chromatographic analysis and found to have a purity of more than 98%, and with 200 g. (1.5 moles) of anhydrous aluminium chloride as the catalyst, and cooled to control the temperature within the range 10—15°C. Then a mixed solution of 214 g. (1.2 moles) of the above 2,6-dimethyl-4-t-butyl phenol and 100 g. of m-xylene was added dropwise, while maintaining the temperature between 10—15°C., and further stirred for an additional four hours to complete the reaction. After the reaction was over, the catalyst was decomposed by adding cold water thereto and the contents were transferred to a separating funnel to remove the water, rinsed three times with water, and then dried over sodium sulphate. The reaction mixture so obtained was treated in the same way as that employed in Example 1 to give 185 g. (1.14 moles) of 5-t-butyl-m-xylene and 136 g. (1.12 moles) of 2,6-dimethyl phenol, the yields based on 2,6-dimethyl-4-t-butyl phenol being 95% and 93% respectively.

EXAMPLE 3

A four-necked one litre flask fitted with a stirrer was charged with 450 g. (4.24 moles) of 98% m-xylene and 200 g. (1.5 moles) of anhydrous aluminium chloride as the catalyst, and cooled so as to maintain the temperature of the contents at 5—10°C. 220 g. (1.23 moles) of 2,6-dimethyl-4-t-butyl phenol was added gradually. After the 2,6-dimethyl-4-t-butyl phenol had been added, the contents were further stirred for an additional 4 hours while maintaining the temperature at 5—10°C. to complete the reaction. After the reaction was complete, the reaction mixture was combined with cold water to decompose the catalyst, and the contents were transferred to a separating funnel to remove the aqueous phase therefrom. The remaining phase was rinsed three times with water and then dried over sodium sulphate. The reaction mixture thus obtained was distilled to separate a fraction boiling at 136—141°C. (m-xylene) and the remaining portion was further distilled to separate a fraction boiling at 78—85°C./6 mm Hg. The last-mentioned fraction was then transferred to a separating funnel and shaken with an added 600 cc of 10% aqueous sodium hydroxide solution, and allowed to stand to effect separation into aqueous and organic phases. The alkaline aqueous phase so obtained was neutralised with sulphuric acid to separate out white crystals which were filtered by suction, washed with a small amount of water, and vacuum dried to give 143 g. of white crystals. The melt-

ing point of these white crystals was 47—49°C. which showed no depression when mixed with an authentic sample of 2,6-dimethyl phenol having a m.p. of 49°C. The infrared absorption spectrum showed complete agreement with that of 2,6-dimethyl phenol. The yield of 2,6-dimethyl phenol based on 2,6-dimethyl-4-t-butyl phenol was 95%. The organic phase after treatment with 10% aqueous sodium hydroxide solution was washed with water, dried over calcium chloride, and analysed and found to have a refractive index of $n^{20}_D=1.4961$ which was consistant with the refractive index of 5-t-butyl-m-xylene. The infrared absorption spectrum was in complete agreement with that of 5-t-butyl-m-xylene. The yield of 5-t-butyl-m-xylene thus obtained was 185.5 g. corresponding to 93% based on 2,6-dimethyl-4-t-butyl phenol.

EXAMPLE 4

A copper one litre flask fitted with a stirrer was charged with 300 g. (total 2.82 moles) of an ordinary mixed xylene having a composition of 1.2% toluene, 25.2% ethylbenzene, 42.8% m-xylene, 10.6% p-xylene, and 20.2% o-xylene. After cooling the contents to 0°C., they were mixed with 40 g. (2.0 moles) of liquid hydrogen fluoride as catalyst, while shaking. A mixture of 200 g. (1.12 moles) of 2,6-dimethyl-4-t-butyl phenol and 300 g. of mixed xylene was slowly added dropwise, with stirring, while keeping the temperature of the contents within the range 0—5°C. After the dropwise addition was over, the contents were further stirred for an additional four hours while maintaining the temperature at 0—5°C. to complete the reaction.

After the reaction had been completed, the contents were poured on to cracked ice, neutralised with sodium hydrogen carbonate, and dried over anhydrous sodium sulphate.

The reaction mixture obtained in this way was treated in a manner similar to the method of Example 1, to give 131 g. of 2,6-dimethyl phenol the yield of which, based on 2,6-dimethyl-4-t-butyl phenol, was 96%.

EXAMPLE 5

5-t-amyl-m-diethlybenzene obtained according to the procedure of Reference Example 4 (t-amylation of m-diethylbenzene with t-amyl alcohol) was sulphonated as in Example 1 to give sodium 2,6-diethyl-4-t-amyl benzene sulphonate. The yield of this product based on 5-t-amyl-m-diethylbenzene was 96%.

Next, a 400 cc nickel crucible was charged with 281 g. (5 moles) of potassium hydroxide and 30 cc water and heated to an internal temperature of 300°C. At this time, 62 g. (0.2 mole) of the powdered sodium 2,6-diethyl-4-t-amyl benzene sulphonate obtained in the above procedure was added little by little and reacted and treated as in Example 1 to give 34.8 g. of crystals of 2,6-diethyl-4-t-amyl phenol, the yield of which based on sodium 2,6-diethyl-4-t-amyl benzene sulphonate was 79%.

Into a four-necked one litre flask fitted with a stirrer, were charged 570 g. (4.25 moles) of m-diethylbenzene and 267 g. (1.0 mole) of anhydrous aluminium bromide as the catalyst. While maintaining the temperature of the contents at 5—10°C., 264 g. (1.2 moles) of 2,6-diethyl-t-amyl phenol obtained previously was slowly added with stirring.

Thereafter, the reaction and treatment were carried out as in Example 3 to give 171 g. (1.14 moles) of 2,6-diethyl phenol and 233 g. of 5-t-amyl-m-diethyl benzene; these were obtained in yields of 95% and 95% based on 2,6-diethyl-4-t-amyl phenol, respectively.

EXAMPLE 6

A 500 cc four-necked flask fitted with a stirrer, was charged with 162 g. (1 mole) of 5-t-butyl-m-xylene obtained by the procedure of Reference Example 1, 12.7 g. (0.05 mole) of iodine as catalyst and 300 cc of carbon tetrachloride as solvent. While maintaining the temperature of the contents at 5°C., gaseous chlorine in an approximately equimolar amount was introduced with stirring. After allowing the contents to stand for an additional two hours at 5—10°C. to complete the reaction, they were distilled to separate a fraction boiling 105—107°C./5—10 mm Hg. which was then cooled to form 127 g. (0.65 mole) of needle crystals. The crystals so obtained showed a chlorine content of 17.83% and were identified to be 2-chloro-5-t-butyl-m-xylene by infrared absorption spectrum analysis. The yield based on the 5-t-butyl-m-xylene was 65%.

98.3 g. (0.5 mole) of the 2-chloro-5-t-butyl-m-xylene and 200 cc of 15% aqueous sodium hydroxide solution were introduced into a one litre rocking autoclave, and reacted at 320°C. under a nitrogen pressure of 300 atm. for 8 hours with shaking. After this the reaction mass was acidified with sulphuric acid to separate

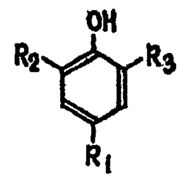
out white crystals which were then filtered by suction and vacuum dried to give 73.0 g. (0.41 mole) of white crystals having a melting point of 79.5—80.5°C. The infrared absorption spectrum completely agreed with that of 2,6-dimethyl-4-t-butyl phenol. The yield of 2,6-dimethyl-4-t-butyl phenol based on 2-chloro-5-t-butyl-m-xylene was 82%.

191 g. (1.8 moles) of m-xylene was added to a four-necked 500 cc flask made of fluorine-containing resin and fitted with a stirrer, and cooled to 0°C. by using an ice bath. 50 g. (2.5 moles) of liquid hydrogen fluoride and 33.9 g. (0.5 mole) of boron trifluoride, as catalyst, were added and thoroughly mixed. Then, a mixture of 89 g. (0.5 mole) of 2,6-dimethyl-4-t-butyl phenol obtained in the above procedure and 53 g. (0.5 mole) of m-xylene were added dropwise, with stirring, while maintaining the temperature of the contents at 0°C. and the reaction was completed by continuously stirring the resultant mixture for an additional 4 hours after the addition had been completed.

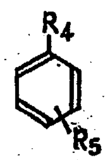
Thereafter, the treatment was carried out as in Example 1 to give 77.8 g. (0.48 mole) of 5-t-butyl-m-xylene and 58.5 g. (0.48 mole) of 2,6-dimethyl-phenol, the yields of which were both 96% based on 2,6-dimethyl-4-t-butyl phenol.

WHAT WE CLAIM IS:—

1. A process for the production of a 2,6-dialkyl phenol which comprises reacting a 2,6-dialkyl-4-t-alkyl phenol having the formula



with an aromatic hydrocarbon having the formula



in the presence of a Friedel-Crafts catalyst at a temperature from −20 to 100°C to transfer the t-alkyl group to said aromatic hydrocarbon, wherein R_1 denotes a C_{4-7} t-alkyl group, R_2 and R_3 each denotes a C_{1-4} normal alkyl group, and R_4 and R_5 each denotes either hydrogen or a C_{1-4} normal alkyl group located mutually in o- or m-position when neither R_4 nor R_5 is hydrogen.

2. A process as claimed in Claim 1, in which said 2,6-dialkyl-4-t-alkyl phenol is 2,6-dimethyl-4-t-butyl phenol.

3. A process as claimed in Claim 1 or Claim 2, in which said aromatic hydrocarbon is m-xylene.

4. A process as claimed in Claim 1 or Claim 2, in which the aromatic hydrocarbon is a mixed xylene comprising substantially m-xylene, o-xylene, p-xylene, and ethylbenzene.

5. A process as claimed in any of the preceding Claims, in which the Friedel-Crafts catalyst is boron trifluoride, anhydrous aluminium chloride, anhydrous aluminium bromide, hydrogen fluoride, or a mixture thereof.

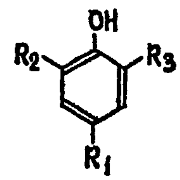
6. A process as claimed in any of the preceding Claims, in which the amount of the Friedel-Crafts catalyst to be used per mole of said 2,6-dialkyl-4-t-alkyl phenol is 0.2 to 6.0 moles.

7. A process as claimed in any of the preceding Claims, in which the amount of said aromatic hydrocarbon to be used per mole of said 2,6-dialkyl-4-t-alkyl phenol is 1 to 10 moles.

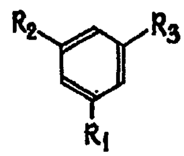
8. A process as claimed in Claim 7, in which the reaction temperature is within the range of from −20°C to +30°C.

9. A process as claimed in Claim 8, in which the reaction temperature is within the range of from −5°C to +15°C.

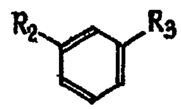
10. A process for the production of a 2,6-dialkyl phenol which comprises a first step in which a 2,6-dialkyl-4-t-alkyl phenol having the formula



is prepared from a 1,3-dialkyl-5-t-alkyl benzene having the formula



a second step in which the 2,6-dialkyl-4-t-alkyl phenol is reacted with a 1,3-dialkyl benzene having the formula



in the presence of a Friedel-Crafts catalyst at a temperature from −20 to 100°C to form a 2,6-dialkyl phenol and a 1,3-dialkyl-5-t-alkyl benzene, and circulating the 1,3-dialkyl-5-t-alkyl benzene obtained in the second step to the first step for reuse, wherein R_1 denotes a C_{4-7} t-alkyl group, and R_2 and R_3 each denotes a C_{1-4} normal alkyl group.

11. A process as claimed in Claim 10, in which in the first step 1,3-dialkyl-5-t-alkyl benzene is sulphonated to form 2,6-dialkyl-4-t-alkyl sulphonic acid followed by alkali fusion to obtain said 2,6-dialkyl-4-t-alkyl phenol.

12. A process as claimed in Claim 11, in which the sulphonating agent is concentrated sulphuric acid, fuming sulphuric acid, or a mixture thereof.

13. A process as claimed in Claim 11 or Claim 12, in which the amount of the sulphonating agent to be used is 0.5 to 3.0 moles per mole of said 1,3-dialkyl-5-t-alkyl benzene.

14. A process as claimed in any of Claims 11 to 13, in which the temperature of the sulphonation is within the range of 20 to 90°C.

15. A process as claimed in any of Claims 11 to 14, in which the 2,6-dialkyl-4-t-alkyl sulphonic acid is subjected to alkali fusion with potassium hydroxide or with a mixture of sodium hydroxide and potassium hydroxide.

16. A process as claimed in any of the Claims 11 to 15, in which the amount of alkali hydroxide to be used in the alkali fusion of the 2,6-dialkyl-4-t-alkyl sulphonic acid is 5—25 moles per mole of the 2,6-dialkyl-4-t-alkyl sulphonate.

17. A process as claimed in any of the Claims 11 to 16, in which the alkali fusion of the 2,6-dialkyl-4-t-alkyl sulphonic acid is carried out at a temperature of 310 to 400°C.

18. A process as claimed in Claim 17, in which the alkali fusion of the 2,6-dialkyl-4-t-alkyl sulphonic acid is carried out at a temperature of 330 to 350°C.

19. A process as claimed in any one of Claims 11 to 18, in which the alkali fusion of the 2,6-dialkyl-4-t-alkyl sulphonic acid is carried out in an atmosphere of nitrogen.

20. A process as claimed in Claim 10, in which in the first step said 1,3-dialkyl-5-t-alkyl benzene is chlorinated to form 2,6-dialkyl-4-t-alkyl chlorobenzene followed by hydrolysis to the 2,6-dialkyl-4-t-alkyl phenol.

21. A process as claimed in Claim 20, in which said 1,3-dialkyl-5-t-alkyl benzene is chlorinated by gaseous chlorine.

22. A process as claimed in Claim 20 or Claim 21, in which said 1,3-dialkyl-5-t-alkyl benzene is chlorinated using 0.01 to 1 mole of a nuclear chlorinating catalyst per mole of the 1,3-dialkyl-5-t-alkyl benzene.

23. A process as claimed in any of Claims 20 to 22, in which said 1,3-dialkyl-5-t-alkyl benzene is chlorinated in the presence of iodine.

24. A process as claimed in any of the Claims 20 to 23, in which the 2,6-dialkyl-4-t-alkyl chlorobenzene is hydrolyzed with an aqueous solution of an alkali hydroxide to obtain said 2,6-dialkyl-4-t-alkyl phenol.

25. A process as claimed in Claim 24, in which the 2,6-dialkyl-4-t-alkyl chlorobenzene is hydrolyzed with 10 to 15 wt.% of aqueous alkali hydroxide solution.

26. A process as claimed in any of the Claims 10 to 25, in which said 1,3-dialkyl-5-t-alkyl benzene is 5-t-butyl-m-xylene, and said 2,6-dialkyl-4-t-alkyl phenol is 2,6-dimethyl-4-t-butyl phenol, and said 1,3-dialkyl benzene is m-xylene.

27. A process as claimed in Claim 26, in which the reaction temperature of said second step is within the range of −20°C to +30°C.

28. A process as claimed in Claim 27, in which the reaction temperature of said second step is within the range of from −5°C to +15°C.

29. A process as claimed in any of the Claims 10 to 28, in which the Friedel-Crafts catalyst used in the second step comprises boron trifluoride, anhydrous aluminium chloride, anhydrous aluminium bromide, hydrogen fluoride, or a mixture thereof.

30. A process as claimed in any of Claims 10 to 29, in which the amount of the Friedel-Crafts catalyst used is 0.2 to 6.0 moles per mole of said 2,6-dialkyl-4-t-alkyl phenol.

31. A process as claimed in any of the Claims 10 to 30, in which the amount of the 1,3-dialkylbenzene used is 1 to 10 moles per mole of said 2,6-dialkyl-4-t-alkyl phenol.

32. A process as claimed in any of the preceding Claims, in which R_1 is a t-butyl group.

33. A process for the production of a 2,6-dialkyl phenol according to any of the preceding claims, substantially as hereinbefore described with reference to the Examples of the invention.

34. A 2,6-dialkyl phenol wherever prepared by a process as claimed in any of the preceding Claims.

35. A 1,3-dialkyl-5-t-alkyl benzene wherever prepared by a process as claimed in any of the Claims 10 to 32.

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